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Inventor(s): Jerold S. Horn and James D. Hansen
Title: FLUOROPOLYMERIC ORTHODONTIC ARTICLE

- ☒ Enclosed is the above-mentioned new patent application. It includes 9 sheet(s) of drawings.
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- ☒ Enclosed are an application assignment to Minnesota Mining and Manufacturing Company and a completed Assignment Recordation Cover Sheet.
- ☐ Enclosed is _____.
- ☒ The fee for filing the application is computed as follows:

| Claims As Filed | | | | |
|---|---------------------|---------------------|-------------|----------------------------|
| (1) For | (2) Number Filed | (3) Number Extra | (4) Rate | (5) Basic Fee \$760. |
| Total Claims | 27 -20 = | 7 | x \$18. | \$126.00 |
| Independent Claims | 4 -3 = | 1 | x \$78. | \$78.00 |
| Additional fee for filing one or more multiple dependent claims | | | \$260. | \$0.00 |
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FLUOROPOLYMERIC ORTHODONTIC ARTICLE

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Background of the Invention

This invention relates to fluoropolymeric orthodontic articles.

Orthodontic treatment often involves the application of mechanical forces to urge improperly positioned teeth into correct alignment. One common form of orthodontic treatment includes the use of orthodontic brackets affixed to the surface of a
10 tooth, and a resilient curved arch wire seated in slots on the brackets. The arch wire exerts a restoring force on the teeth which tends to shift the teeth into orthodontically correct alignment.

Orthodontic articles such as, e.g., brackets, were traditionally formed from metal, but more recently have been formed from plastic and ceramic. Plastic brackets can
15 be fabricated to be translucent to transparent in character relative to metal brackets. It is often difficult, however, to maintain the aesthetic characteristics of plastic brackets during use because food and beverages can stain and discolor the brackets while they reside in a patient's mouth.

Summary of the Invention

20 In one aspect, the invention features an orthodontic article (e.g., an orthodontic bracket) that includes a fluoropolymer and that exhibits at least about 0.001 % transmittance at 546 nm when measured according to the Transmittance Test Procedure described herein. In another embodiment, the article exhibits at least about 0.01 % transmittance at 546 nm when measured according to the Transmittance Test
25 Procedure. In other embodiments, the article exhibits a transmittance of at least about 0.001% over a wavelength range of from 400 nm to 800 nm when measured according to the Transmittance Test Procedure.

component. In one embodiment, the method further includes contacting the polymerized component treated surface with an adhesive composition.

In another aspect the invention features an orthodontic article that includes a fluoropolymer selected from the group consisting of perfluoroethylene-propylene copolymer, perfluoroalkoxyethylene, ethylene-tetrafluoroethylene copolymer, polyvinylidene fluoride, polyvinyl fluoride, polychlorotrifluoroethylene, ethylene-chlorotrifluoroethylene copolymer, and combinations thereof. In one embodiment, the orthodontic article includes a bracket. The orthodontic article may further include a metallic component.

In another aspect, the invention features a kit for adhering an orthodontic article to a tooth. The kit includes an orthodontic article that includes a fluoropolymer having at least about 0.001% transmittance at 546 nm when measured according to the Transmittance Test Procedure; and an adhesive system that includes a) a polymerizable component; and b) an organoborane amine complex. In one embodiment, the organoborane amine complex is disposed on a surface of the orthodontic article. In another embodiment, the kit further includes a polyimide film.

The orthodontic articles are resistant to staining by food and beverages such as mustard and spaghetti sauce such that the article remains aesthetically pleasing in appearance and does not unduly darken or turn yellow during the time the article remains in the oral cavity. The orthodontic articles also maintain their essentially translucent to transparent character over the useful life of the article such that they transmit the color of the underlying tooth surface to which they are adhered.

Other features and advantages of the invention will be apparent from the following description of the preferred embodiments thereof, and from the claims.

Brief Description of the Drawing

FIG. 1 is a front view looking toward a buccolabial side (i.e., toward a lip or cheek facing side) of an orthodontic bracket;

Description of the Preferred Embodiments

Orthodontic articles are capable of being mounted on a tooth, and are used to transmit to the tooth a corrective force from an arch wire, spring, elastic, or other activatable force-applying component.

5 FIGS. 1 and 2 show an exemplary orthodontic article in the form of an orthodontic bracket 10. The bracket has a base 11 suitable for either direct bonding to a tooth or attachment to any kind of mounting fixture. A tooth facing surface 12 of the base 11 can be concavely curved about both mesiodistal axis and an apical axis to match the natural convexity of the tooth labial surface, but other curvatures or flat surfaces can
10 also be used to accommodate bracket positioning. A bracket body 13 extends from base 11 to define bracket tie-wings 14 for ligature anchorage, and a mesiodistally oriented arch-wire slot 15 extending from an outer body surface 16 into the bracket body.

 FIGS. 3 and 4 depict a second embodiment of an orthodontic bracket 20 as seen from the buccolabial side and from the end, respectively. FIGS. 5 and 6 depict a test
15 article 30 in which a slot 35 is seen from the top in FIG. 5. The article is shown in perspective side view in FIG. 6. The test article of FIGS. 5 and 6 approximates the overall size and thickness of a conventional orthodontic bracket.

 The fluoropolymeric orthodontic articles described herein are resistant to staining during use such that the articles maintain their original color as determined by
20 the unaided human eye under common lighting conditions (e.g., sunlight and incandescent light). The fluoropolymeric orthodontic articles are resistant to staining from oil-based staining agents such as, e.g., spaghetti sauce, and water-based staining agents such as, e.g., mustard. Preferably the fluoropolymeric orthodontic articles exhibit a Delta E color shift of less than 2 (more preferably less than 1, and most preferably 0)
25 when tested according to the hydrophilic color shift test procedure set forth below, and a Delta E color shift of less than 5 (more preferably less than 3, and most preferably 0) when tested according to the oleophilic color shift test procedure set forth below.

The orthodontic articles appear translucent to transparent to the human eye such that when the article is placed on a surface such as, e.g., a tooth, the article transmits the color of the underlying surface through the article. Preferably the article exhibits at least about 0.001% transmittance at 546 nm, more preferably 0.01% transmittance at 546 nm when measured according to the Transmittance Test Procedure set forth below. Preferred articles exhibit a transmittance of at least about 0.001% over the wavelength range of 400 nm to 800 nm when measured according to the Transmittance Test Procedure.

The fluoropolymeric orthodontic articles include fluoropolymer resins that are capable of being hardened and have sufficient strength, hydrolytic stability, and non-toxicity to render them suitable for use in the mouth. The fluoropolymers are translucent to transparent. Preferred fluoropolymers exhibit at least about 0.001% transmittance, more preferably 0.01% transmittance, at 546 nm when measured according to the Transmittance Test Procedure. Useful fluoropolymers include perfluoroethylene-propylene copolymer, perfluoroalkoxyalkane, ethylene-tetrafluoroethylene copolymer, polyvinylidene fluoride, polyvinyl fluoride, polyfluorotrifluoroethylene, ethylene-chlorotrifluoroethylene copolymer, and combinations thereof.

Examples of useful commercially available fluoropolymers include: Tefzel HT 2004 ethylene-tetrafluoroethylene copolymer including glass fibers, Tefzel 200, Tefzel 220, Tefzel 280, Tefzel 210, HT 2055, HT 2055NA, HT 2088NA, HT 2098, HT 2118, HT 2141, HT 2155 and HT 2158 ethylene-tetrafluoroethylene copolymers, Teflon PFA 340 perfluoroalkoxy fluorocarbon resin, and Teflon AF 1600 and Teflon AF 2400 perfluoro(2,2-dimethyl-1,3-dioxole)-tetrafluoroethylene copolymer (all available from DuPont); Hyflon PFA tetrafluoroethylene-perfluorovinylether copolymer, and Halar, Halar 300 and Halar 500 DA ethylene-chlorotrifluoroethylene copolymer (all available from Ausimont); Kel-F 81 PCTFE polychlorotrifluoroethylene (available from Minnesota

Mining and Manufacturing), and the line of fluoropolymers available under the trade designation "THV" from Dyneon, LLC (Oakdale, Minnesota).

Preferred adhesive systems for bonding a fluoropolymeric article to a tooth surface include a primer composition and a polymerizable component. The primer composition is capable of enabling or enhancing the adhesion of a fluoropolymeric article to the surface of a tooth. Useful primer compositions include an organoborane amine complex capable of initiating polymerization of a polymerizable component. The polymerizable component may include, e.g., monomers, oligomers, and combinations thereof that are capable of polymerizing and thereby forming an adhesive composition.

Preferred adhesive systems also include an effective amount of a compound that is reactive with or will remove the amine portion of the organoborane amine complex so as to liberate the organoborane and thereby allow the organoborane to initiate polymerization of polymerizable components.

Examples of useful organoborane amine complexes and adhesive systems that include an organoborane amine complex are described, e.g., in U.S. Patent Nos. 5,539,070 (Zharov et al.), 5,616,796 (Pocius et al.), 5,681,910 (Pocius), and 5,310,835 (Skoultchi et al.), and in WO 98/17694 and WO 97/07151, each of which is incorporated herein.

The fluoropolymeric orthodontic article, the tooth, or a combination thereof, can be treated (i.e., primed) with a primer composition prior to adhering the article to the tooth. One example of a useful priming composition is Transbond XT Light cure priming composition (Minnesota Mining and Manufacturing ("3M"), St. Paul, MN). Other useful priming compositions are described in U.S. Patent No. 5,558,516 (Horn et al.) and incorporated herein. The above-described organoborane amine adhesive compositions are also suitable priming compositions.

One example of a useful method for adhering the fluoropolymeric orthodontic article to the surface of a tooth includes contacting the orthodontic article with an

adhesive composition and adhering the orthodontic article to the tooth surface. The method can include priming a surface, e.g., the surface of the tooth, the orthodontic article, and combinations thereof, with a priming composition prior to adhering the orthodontic article to the surface of the tooth. The surface can be primed with one or
5 more priming compositions sequentially, simultaneously and in combinations thereof. In one preferred method, the surface is primed with a composition that includes an organoborane amine complex. In another preferred method, the surface can be pretreated, e.g., primed, and then packaged for later use as described, for example, in U.S. Patent No. 5,558,516 (Horn et al.) and incorporated herein. After pretreatment, the
10 surface can be treated with a primer composition, an adhesive composition and combinations thereof.

EXAMPLES

Transmittance Test Procedure

The % transmittance of light through an article is measured as follows. An
15 article is placed in the well of a glass well slide such that the tooth contacting surface of the article is in contact with the slide. The well is filled with immersion liquid having a refractive index ("ND") of 1.515 and covered with a coverslip. The bracket containing slide is then placed under a microscope having a 3.2x objective, a numerical aperture ("N.A.") of 0.06, and a substage condensing lens system having a 0.3 N.A. The aperture
20 and field diaphragms on the substage condensor are set up to produce the standard transparency by transmission measurement configuration (t(o/180)) of ASTM E-179-91a "Standard Guide for the Selection of Geometric Conditions for Measurement of Reflection and Transmission Properties of Materials."

The area of the article that is of interest is then brought into focus. The slide
25 is then moved such that a reference area is brought into view (the focus of the microscope is not changed during this procedure). The reference area is an area within the well that contains immersion oil but does not contain the article. A calibration spectrum is

collected from the reference area and is defined as having a transmittance of 1.0 over the wavelength range. The slide is then moved such that the area of interest of the article is brought into the field of view and the transmittance spectrum is collected over a predetermined wavelength or wavelength range e.g., 400 nm to 800 nm.

5 A series of measurements are taken at a number of locations on the article that are visible to an observer when the article is worn by a user, see, e.g., the numbers and letters indicated on FIGS. 3, 4, 5, 6 and 13. The measurements are taken in a labial-lingual direction along paths that extend from the labial-most surface of the article to the lingual-most base of the article, being careful to avoid areas in which a metal object is
10 present in the article and would interfere with the path of the beam of radiation. The lowest transmittance value obtained for the article at a given wavelength is the transmittance of the article at that wavelength.

Color Measurement and Calculation Test Procedure

15 The color shift in an article is measured as follows. A LABSPHERE certified diffuse white reflectance standard (CSS-99-010 8812A) is placed on the stage of a Leitz Orthoplan Microscope equipped with a Leitz MPV-SP Spectrophotometer illuminated with a tungsten halogen lamp. The microscope is set to 3.2x objective with a numerical aperture ("N.A.") of 0.06. A fiber optic ring, which produces a 45 degree cone of
20 illumination, is mounted on the objective lens of the microscope producing a standard 45° illumination/ 0° detection color measurement (R(45/0)) according to ASTM E-179-91a, "Standard Guide for the Selection of Geometric Conditions for Measurement of Reflection and Transmission Properties of Materials."

The spectrophotometer is set to a measuring spot of 1mm x 1mm, slit width of
25 6 nm, threshold of 1, high voltage of 480v, filter edge 100Hz, and integration 8x. Two scans are taken from 370 nm to 800 nm at a sampling rate of 1/3 nm and data is reported every 1 nm.

The lamp intensity of the halogen lamp is adjusted such that the signal is never greater than 90% of that needed to saturate the detector. A calibration spectrum is collected from the area and is defined as having a reflectivity of 100% over the wavelength range. The reflectance standard is removed and a sample is placed on the microscope stage. An area of interest is brought into crisp focus and a reflectance spectrum is collected. The reflectance standard is returned to the microscope stage, brought into focus and the reflectance spectrum is collected. If the spectrum collected is other than 100% for the second measurement of the standard over the wavelength range, the standardization steps are repeated.

The color measurements and calculations are performed in accordance with ASTM standards E-308-95, "Standard Practice for Computing the Colors of Objects by Using the CIE System," and D 2244-93, "Standard Test Method for Calculation of Color Differences from Instrumentally Measured Color Coordinates" using the L*a*b* color representation. The L* value is a measure of the brightness of the sample. The a* is a measure of the redness for a positive value or greenness for a negative value, and b* is a measure of yellowness for a positive value or blueness for a negative value. Color differences (i.e., ΔL^* , Δa^* and Δb^*) are calculated by subtracting the reference value from the sample value. The total color shift is represented by delta E according to the following formula:

$$\Delta E = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}}$$

Hydrophilic Color Shift Test Procedure

The color shift exhibited by an article after contact with a hydrophilic substance is measured as follows. Specimens are immersed for one hour at 60°C in French's 100% pure prepared yellow mustard. The samples are then removed, rinsed thoroughly with water, and air-dried.

The samples are then tested according to the above Color Shift Measurement and Calculation Test Procedure to determine Delta E.

Oleophilic Color Shift Test Procedure

5 The color shift exhibited by an article after contact with an oleophilic substance is measured as follows. Specimens are immersed for 2.5 hours at 60°C in Ragu Old World Style Flavored Spaghetti sauce with meat. The samples are then removed, rinsed thoroughly with water, and air-dried. The samples are then tested according to the above Color Shift Measurement and Calculation Test Procedure to
10 determine Delta E.

Staining Test Procedure

Example 1

 A 1 cm x 1 cm x 3 mm sample of Ausimont PFA 450 perfluoroalkoxy
15 fluorocarbon resin (Ausimont) was immersed in French's mustard for period of two weeks at 60°C. The sample was then removed, washed with water, dried and adhered onto a white paper chart. Visual observations regarding the degree of staining were made and recorded. The results are summarized in Table I.

 Additional samples of the Ausimont PFA 450 were immersed in either Ragu
20 spaghetti sauce, chili powder (Spice Island) at 1g per 10g water, or curry powder (Shilling) at 1g per 10g water. The samples remained in the staining agents for two weeks at 60°C. After two weeks the samples were removed, washed with water, and adhered to a chart. Visual observations regarding the degree of staining were made and recorded. The results are summarized in Table I.

Example 2

1 cm x 1 cm x 3 mm samples of Ausimont Halar polyethylene-chlorine trifluoroethylene were stain tested as in Example 1. No staining was observed.

5 Example 3

1 cm x 1 cm x 3 mm samples of DuPont PFA 340 perfluoroalkoxy fluorocarbon resin (DuPont) were stain tested as in Example 1. No staining was observed.

10 Example 4

1 cm x 1 cm x 3 mm samples of Tefzel 210 ethylene-tetrafluoroethylene (DuPont) were stain tested as in Example 1. No staining was observed for the samples immersed in spaghetti sauce, mustard, and chili. A very light yellow was observed for the sample immersed in curry.

15

Example 5

1 cm x 1 cm x 3 mm samples of Tefzel 280 ethylene-tetrafluoroethylene (DuPont) were stain tested as in Example 1. No staining was observed.

20

The results obtained in Examples 1-5 are summarized in Table I.

TABLE I

| Sample | Spaghetti Sauce | Mustard | Chili | Curry |
|-----------|-----------------|---------|-------|-----------------|
| Example 1 | None | None | None | None |
| Example 2 | None | None | None | None |
| Example 3 | None | None | None | None |
| Example 4 | None | None | None | v. Light yellow |
| Example 5 | None | None | None | None |

Bond Strength Test Method

Samples are adhered to a knurled steel ring and immersed in a 37°C water bath for 16-24 hours. The ring with bonded samples is removed from the water, air-dried, and then placed onto the test fixture of an Instron Universal tensile test equipment.

- 5 A wire loop is placed into the upper jaw of the test fixture and through the sample such that it is affixed to the sample. The wire is then pulled by the upper jaw of the test fixture at a rate of 0.2 inches per minute (0.5 cm/min) at a full scale load of 100 lbs (45 kg). The bond strength (in pounds) at separation of the sample from the metal ring is recorded.

10 Primer Composition Preparation

A primer composition was prepared by combining:

- 3.5 parts by weight of a monomer mixture of 39 parts by weight methyl methacrylate, 28 parts by weight butyl acrylate, 3 parts by weight methacrylic acid, 30 parts by weight poly(methylmethacrylate-co-ethyl acrylate (mol. wt. 101,000 (Aldrich)),
15 and 100 parts by weight of a complex of triethylborane and Dytex A 2-methyl-1,5-pentane diamine, having one equivalent of boron per equivalent of nitrogen, and mixing with a wooden stick.

Sample Preparation

20 **Example 6**

- The 0.231 cm x 0.330 cm surface of a 0.231 cm x 0.330 cm x 0.183 cm embossed cube of Halar 500DA ethylene-chlorotrifluoroethylene copolymer (available from Ausimont U.S.A. Inc.) was dipped into the above-described primer composition such that the primer composition completely covered the surface. The primed surface
25 was then pressed against a grooved, knurled steel bonding ring, such that the cube adhered to the bonding ring, and the primer composition was allowed to cure for 48 hours.

The cube was then tested according to the Bond Strength Test Method. The results are reported in Table II.

Example 7

5 A dab of primer composition prepared as described above was coated onto a polyimide film. The 0.231 cm x 0.330 cm surface of a 0.231 cm x 0.330 cm x 0.183 cm embossed cube of Halar 500DA ethylene-chlorotrifluoroethylene copolymer (Ausimont) was dipped into the primer composition such that a face of the cube was completely covered with the primer composition. The primer composition was allowed to cure for
10 48 hours, after which the cube was peeled from the polyimide film. Transbond XT light cure primer composition (3M) was then applied to the primed surface of the cube. The Transbond XT primer was allowed to sit for 60 seconds and then cured with visible light. The primed surface was then coated with Transbond XT light cure adhesive composition (3M), and adhered to a knurled steel bonding ring. The Transbond XT adhesive was then
15 cured by exposing the Transbond XT adhesive to radiation emitted from an Ortholux XT Visible Light Curing Unit for 10 seconds.

The bonded cube was then tested according to the Bond Strength Test Method. The results are reported in Table II.

Example 8

The 0.231 cm x 0.330 cm surface of a 0.231 cm x 0.330 cm x 0.183 cm cube of Halar 500DA ethylene-chlorotrifluoroethylene copolymer (Ausimont) was primed and adhered to a grooved, knurled steel ring according to the method set forth in Example 6.

The bonded cube was then tested according to the Bond Strength Test
25 Method. The results are reported in Table II.

Example 9

The 0.231 cm x 0.330 cm surface of a 0.231 cm x 0.330 cm x 0.183 cm cube of Halar 500DA ethylene-chlorotrifluoroethylene copolymer (Ausimont) was primed and adhered to a grooved, knurled steel ring according to the method set forth in Example 7.

5 The bonded cube was then tested according to the Bond Strength Test Method. The results are reported in Table II.

Example 10

10 A base surface of a test sample in a form depicted in Figs. 5 and 6 made from Teflon PFA340 perfluoroalkoxy fluorocarbon resin (DuPont) was primed and adhered to a grooved, knurled steel ring according to the method set forth in Example 6. The test sample was then tested according to the Bond Strength Test Method. The results are reported in Table II.

Example 11

15 A base surface of a test sample in a form depicted in Figs. 5 and 6 made from Teflon PFA340 was primed and adhered to a grooved, knurled steel ring according to the method set forth in Example 7. The bonded bracket was then tested according to the Bond Strength Test Method. The results are reported in Table II.

20 For Examples 6-11, the bond strength ranged from 7 to 23 pounds ("lbs")/sample with an average of 16 lbs/sample. The failure mode was adhesive between the primer composition and the sample (i.e., the cube or the test sample).

TABLE II

| Example | Bond Strength (lbs) | Standard Deviation |
|---------|---------------------|--------------------|
| 6 | 22 | 3.0 |
| 7 | 5 | 1.4 |
| 8 | 20 | 5.4 |
| 9 | 10 | 3.9 |
| 10 | 13 | 5.3 |
| 11 | 6 | 2.7 |

Example 12

A test sample formed from virgin Halar ethylene-chlorotrifluoroethylene copolymer (Ausimont), having a shape as depicted in FIGS. 5 and 6, was tested according to the Transmittance Test Procedure set forth above. Transmittance was measured through regions identified as 1, 2, 3, 4, 5 and 6 in FIG. 5. The results are shown in % transmittance versus wavelength (nm) in FIG. 7.

Example 13

A bracket made from Halar ethylene-chlorotrifluoroethylene copolymer (Ausimont), having a shape as depicted in FIGS. 3 and 4, was tested according to the Transmittance Test Procedure set forth above. Transmittance data was obtained at locations identified as A, B, C, D, 1, 2 and 3 on FIG. 3. The results are shown in % transmittance versus wavelength (nm) in FIG. 8.

Example 14

A bracket made from Teflon PFA tetrafluoroethylene-perfluorovinylether copolymer (DuPont), having a shape as depicted in FIGS. 3 and 4, was tested according to the Transmittance Test Procedure set forth above. Transmittance data was obtained at locations identified as A, B, C, D, 1, 2 and 3 in FIG. 3. The results are shown in % transmittance versus wavelength (nm) in FIG. 9.

Example 15

A bracket made from Teflon PFA tetrafluoroethylene-perfluorovinylether copolymer (DuPont) having a shape similar to the shape depicted in FIGS. 3 and 4 but with an embedded metallic framework as depicted in FIG. 13, was tested according to the Transmittance Test Procedure set forth above. Transmittance data was obtained at locations identified as A, B, C, D, 1, 2 and 3 in FIG. 13. The results are shown in % transmittance versus wavelength (nm) in FIG. 10.

Example 16

A bracket made from Tefzel 210 ethylene-tetrafluoroethylene copolymer (available from DuPont), having a shape as depicted in FIGS. 3 and 4, was tested according to the Transmittance Test Procedure set forth above. Transmittance data was obtained at locations identified as A, B, C, D, 1, 2 and 3 in FIG. 3. The results are shown in % transmittance versus wavelength (nm) in FIG. 11.

Comparative Example 1

A test article made from Teflon® polytetrafluoroethylene (available from DuPont), having a shape as depicted in FIGS. 5 and 6, was tested according to the Transmittance Test Procedure set forth above. Transmittance data was obtained at locations identified as A, B, 1, 2, 3, 4, 5 and 6 in FIG. 5. The results are shown in % transmittance versus wavelength (nm) in FIG. 12.

Other embodiments are within the claims. For example, the article can be pretreated with a polymerization initiator including, e.g., the above-described organoborane amine complexes, and packaged in a suitable package, e.g., a kit. The articles that have been pretreated with a polymerization initiator can also be provided

with an adhesive precoat and packaged in a suitable package that optionally includes other components necessary to form an adhesive composition.

The article may include a metallic component, e.g., a framework. Orthodontic brackets 20 and 40 including a metal framework 22, 42 depicted by dotted lines are shown in FIGS. 13 and 14. One embodiment of a metallic framework 42 is shown in perspective view in FIG. 15. The metallic framework 22, 42 may be partially or wholly embedded in the body of the bracket 20, 40. The framework can be coated or otherwise colored, e.g., by ink, paint, or porcelain, to match the color of the tooth or the color of the fluoropolymeric material. Examples of a metallic framework are described in U.S. Patent 5,597,302 (Pospisil et al.), which is incorporated herein.

The article may also include a nonfluoropolymeric interior and a fluoropolymeric exterior layer. The fluoropolymeric exterior layer may extend over the entire surface of the nonfluoropolymeric interior or a portion thereof. Examples of suitable nonfluoropolymeric materials include glass, ceramic, plastic (e.g., polycarbonate and polyurethane), or a combination thereof. One example of such an article would include a polycarbonate bracket having an exterior fluoropolymeric layer, and, optionally, an exposed polycarbonate surface, which can be used for bonding the bracket to a tooth. Referring to FIG. 16, an orthodontic bracket 50 having a nonfluoropolymeric interior 52 and a fluoropolymeric layer 54 surrounding a portion of the nonfluoropolymeric interior 52 is shown. Surface 56 of nonfluoropolymeric interior 52 is exposed and is available for bonding to a tooth.

All of the patents, patent applications and test methods cited above are incorporated by reference into this document in total.

What is claimed is:

1. An orthodontic article comprising a fluoropolymer, said article exhibiting at least about 0.001 % transmittance at 546 nm when measured according to the Transmittance Test Procedure.

2. The article of claim 1, wherein said article exhibits a transmittance of at least about 0.001% over a wavelength range of from 400 nm to 800 nm when measured according to the Transmittance Test Procedure.

3. The article of claim 1, wherein said article exhibits a Delta E color shift of no greater than about 2 when tested according to the Hydrophilic Color Shift Test, and a Delta E color shift of no greater than about 5 when tested according to the Oleophilic Color Shift Test.

4. The article of claim 1, wherein said fluoropolymer is selected from the group consisting of perfluoroethylene-propylene copolymer, perfluoroalkoxyethylene, ethylene-tetrafluoroethylene copolymer, polyvinylidene fluoride, polyvinyl fluoride, polychlorotrifluoroethylene, ethylene-chlorotrifluoroethylene copolymer, or a combination thereof.

5. The article of claim 1, wherein said fluoropolymer comprises perfluoroethylene-propylene copolymer.

6. The article of claim 1, wherein said fluoropolymer comprises perfluoroalkoxyethylene.

7. The article of claim 1, wherein said fluoropolymer comprises ethylene-chlorotrifluoroethylene copolymer.

8. The article of claim 1 wherein said article comprises an orthodontic bracket.

9. The article of claim 1, further comprising a polymeric composition disposed on a surface of said article, said polymeric composition comprising an organoborane compound.

10. The article of claim 1, wherein said article exhibits at least about 0.01 % transmittance at 546 nm when measured according to the Transmittance Test Procedure.

11. The article of claim 1, further comprising an organoborane amine complex disposed on a surface of said article.

12. A method for using an orthodontic bracket, said method comprising: contacting a fluoropolymeric orthodontic bracket having an average transmittance of at least 0.001 % when measured according to the Transmittance Test Method with a composition comprising an organoborane compound; and adhering said bracket to a tooth.

13. The method of claim 12, wherein said fluoropolymeric orthodontic bracket exhibits a Delta E color shift of no greater than about 2 when tested according to the Hydrophilic Color Shift Test, and a Delta E color shift of no greater than about 5 when tested according to the Oleophilic Color Shift Test.

14. The method of claim 12, wherein said fluoropolymeric article comprises a fluoropolymer selected from the group consisting of perfluoroethylene-propylene copolymer, perfluoroalkoxyethylene, ethylene-tetrafluoroethylene copolymer, polyvinylidene fluoride, polyvinyl fluoride, polychlorotrifluoroethylene, ethylene-chlorotrifluoroethylene copolymer, or a combination thereof.

15. The method of claim 12, further comprising contacting said surface comprising an organoborane compound with a polymerizable composition, and polymerizing said polymerizable composition to form an adhesive composition.

16. The method of claim 12, further comprising contacting a polyimide film with said composition comprising an organoborane compound prior to adhering said bracket to a tooth.

17. An orthodontic article comprising a fluoropolymer selected from the group consisting of perfluoroethylene-propylene copolymer, perfluoroalkoxyethylene, ethylene-tetrafluoroethylene copolymer, polyvinylidene fluoride, polyvinyl fluoride, polychlorotrifluoroethylene, ethylene-chlorotrifluoroethylene copolymer, or a combination thereof.

18. The article of claim 17, wherein said article comprises a bracket.

19. The article of claim 17, further comprising a metallic component.

20. The article of claim 17, wherein said article exhibits a Delta E color shift of no greater than about 2 when tested according to the Hydrophilic Color Shift Test, and a Delta E color shift of no greater than about 5 when tested according to the Oleophilic Color Shift Test.

5

21. The article of claim 17, wherein said article exhibits at least about 0.001 % transmittance at 546 nm when measured according to the Transmittance Test Procedure.

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22. The article of claim 17, wherein said article exhibits at least about 0.01 % transmittance at 546 nm when measured according to the Transmittance Test Procedure.

15

23. The article of claim 17, wherein said article exhibits at least about 0.001% transmittance over a wavelength range of from 400 nm to 800 nm when measured according to the Transmittance Test Procedure.

20

24. The article of claim 17, further comprising an organoborane amine complex disposed on a surface of said article.

25

25. A kit for adhering an orthodontic article to a tooth, said kit comprising:
an orthodontic article comprising a fluoropolymer having at least about 0.001% transmittance at 546 nm when measured according to the Transmittance Test Procedure; and

an adhesive system comprising

- a) a polymerizable component; and
- b) an organoborane amine complex.

26. The kit of claim 25, wherein said organoborane amine complex is disposed on a surface of said orthodontic article.

5 27. The kit of claim 25, further comprising a polyimide film.

FLUOROPOLYMERIC ORTHODONTIC ARTICLE

Abstract of the Disclosure

Disclosed is an orthodontic article that includes a fluoropolymer and that exhibits at least about 0.001 % transmittance at 546 nm when measured according to the Transmittance Test Procedure.

15921.M11

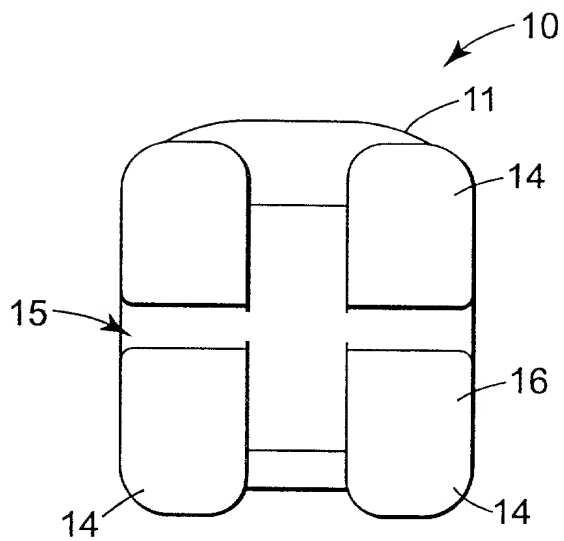


Fig. 1

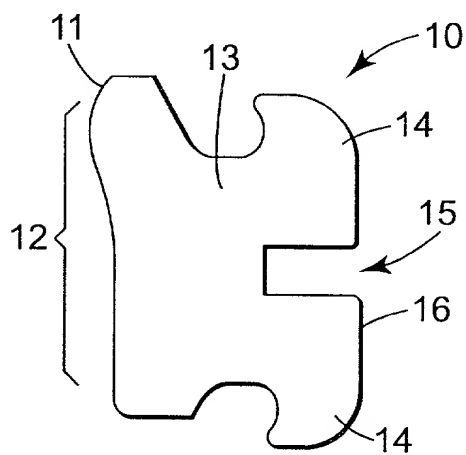


Fig. 2

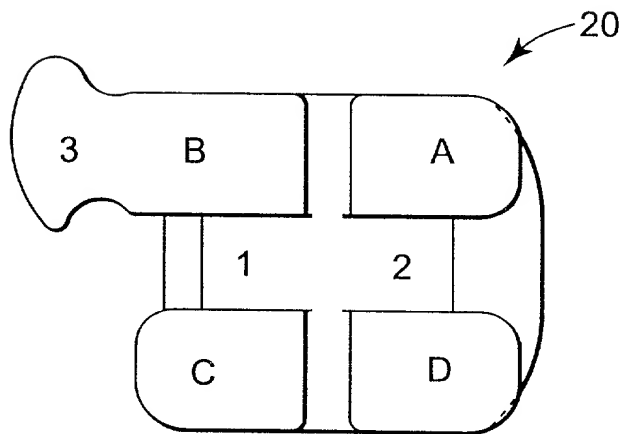


Fig. 3

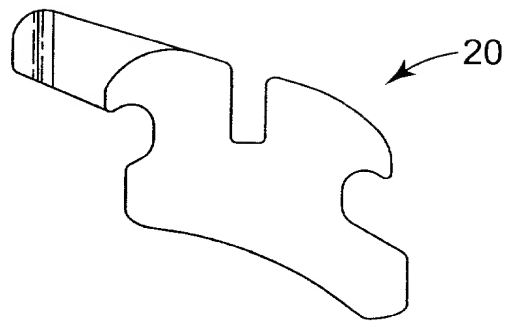


Fig. 4

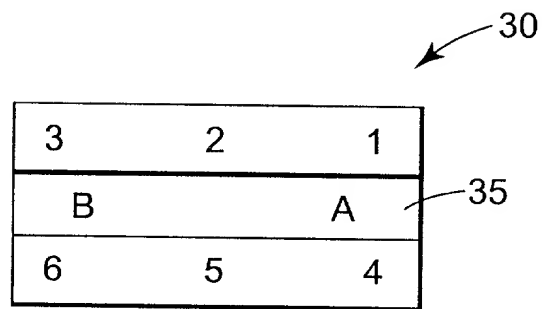


Fig. 5

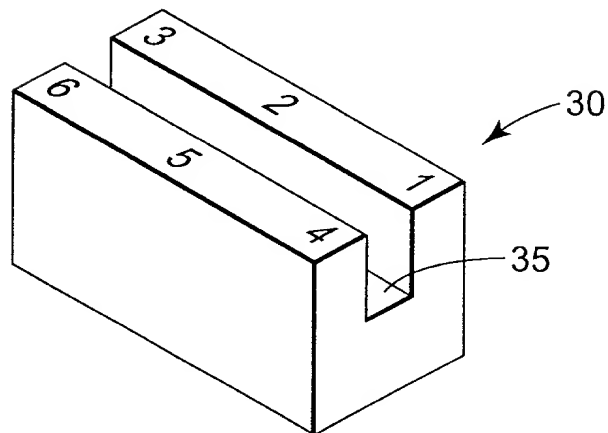


Fig. 6

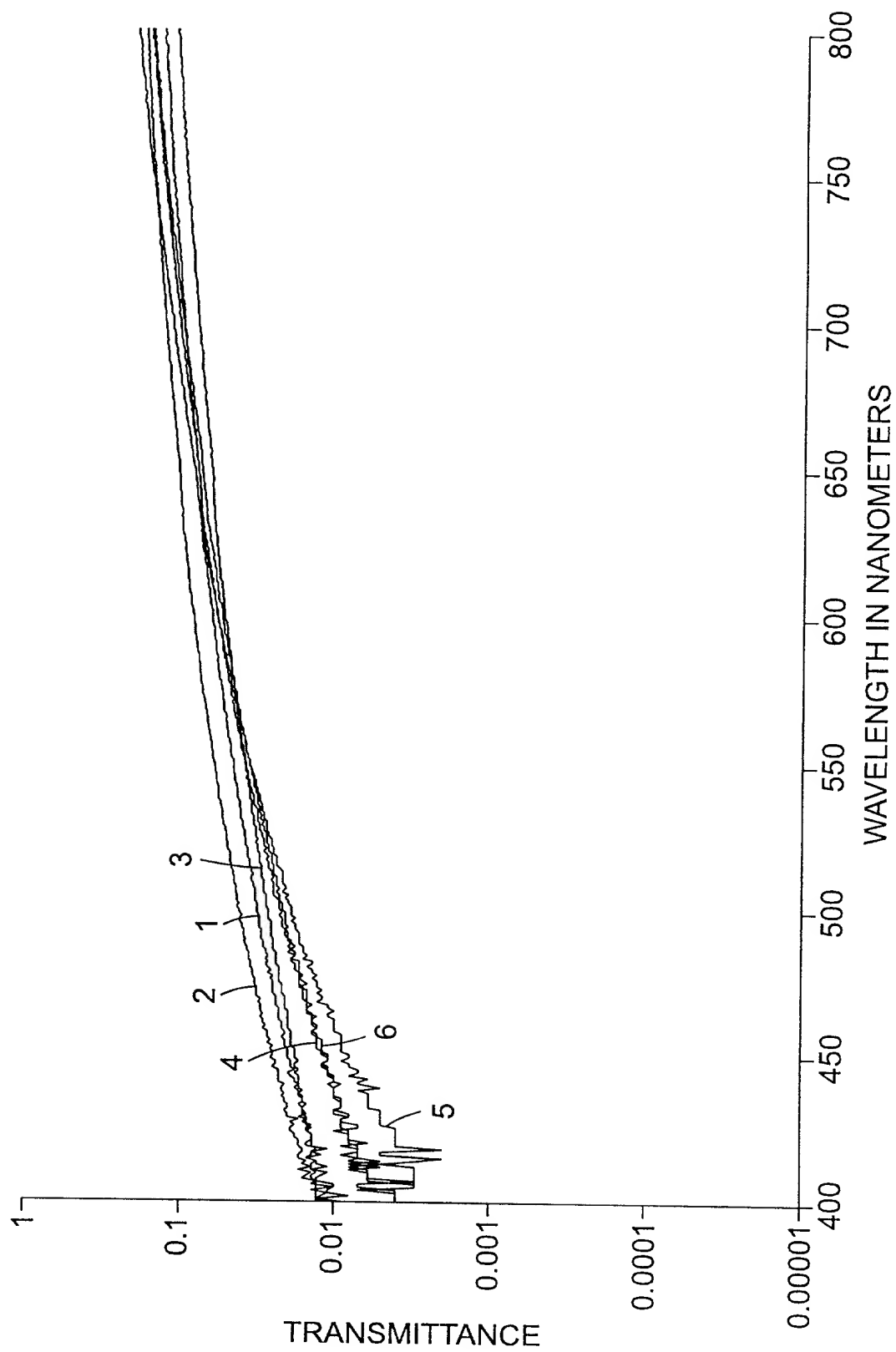


Fig. 7

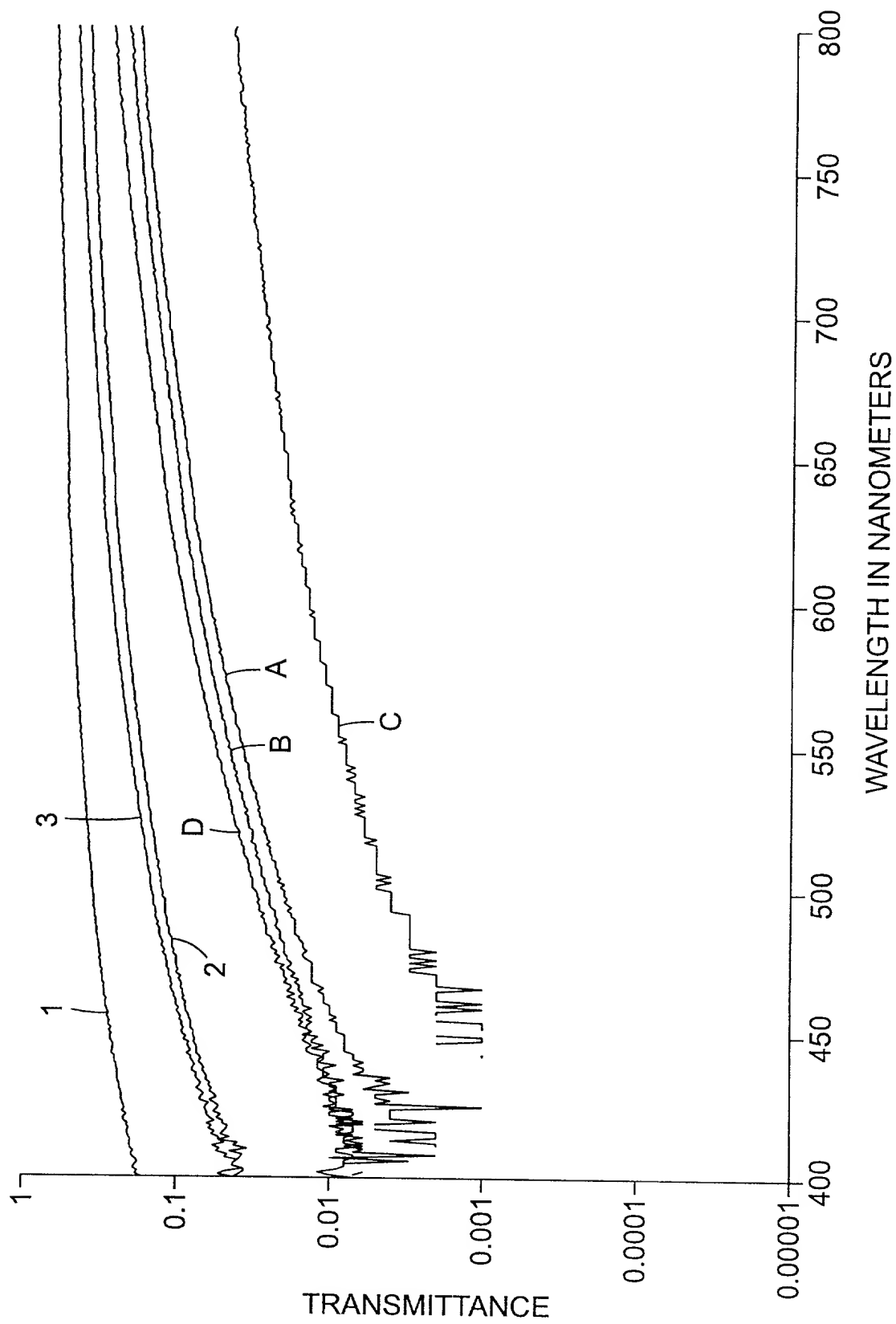


Fig. 8

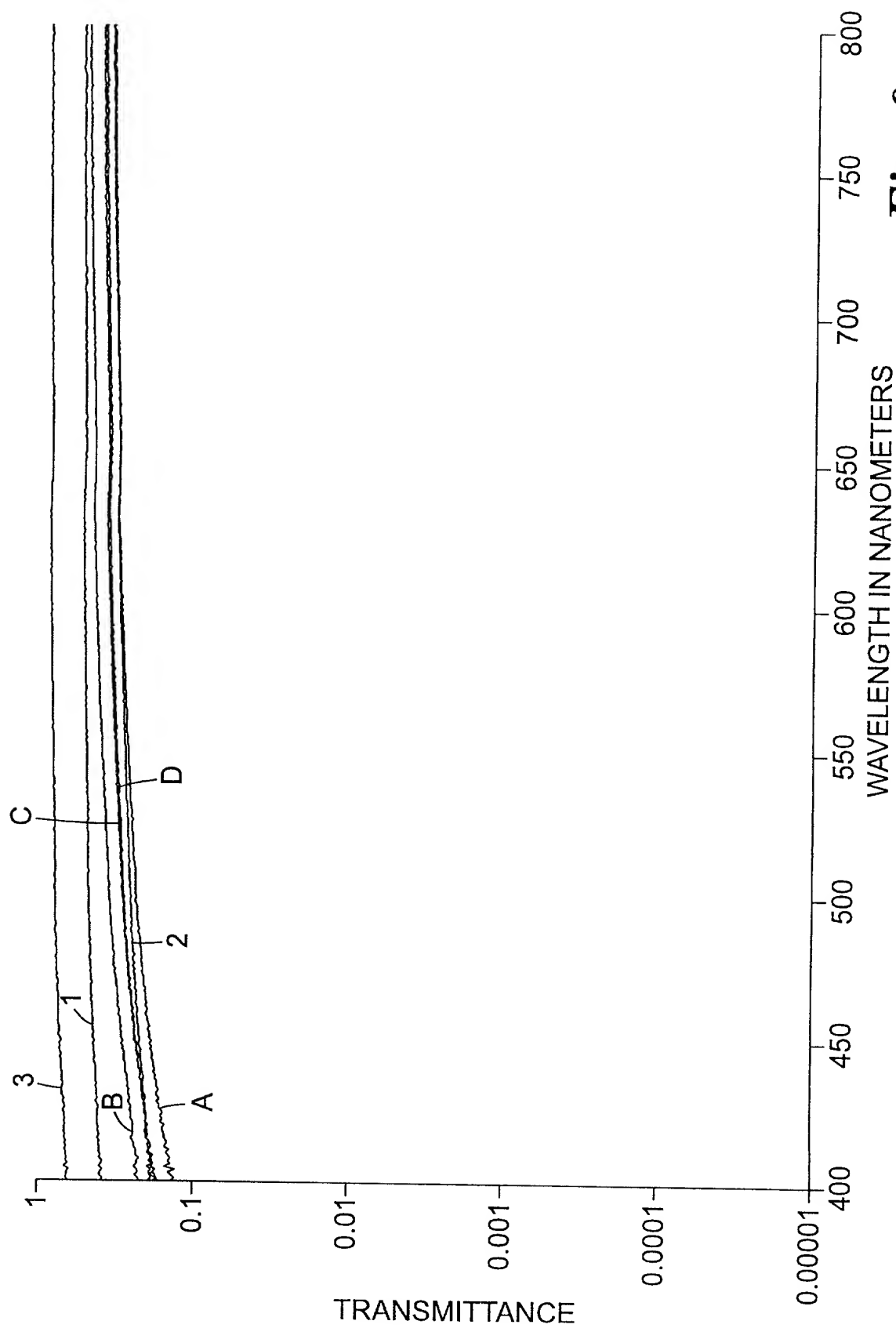


Fig. 9

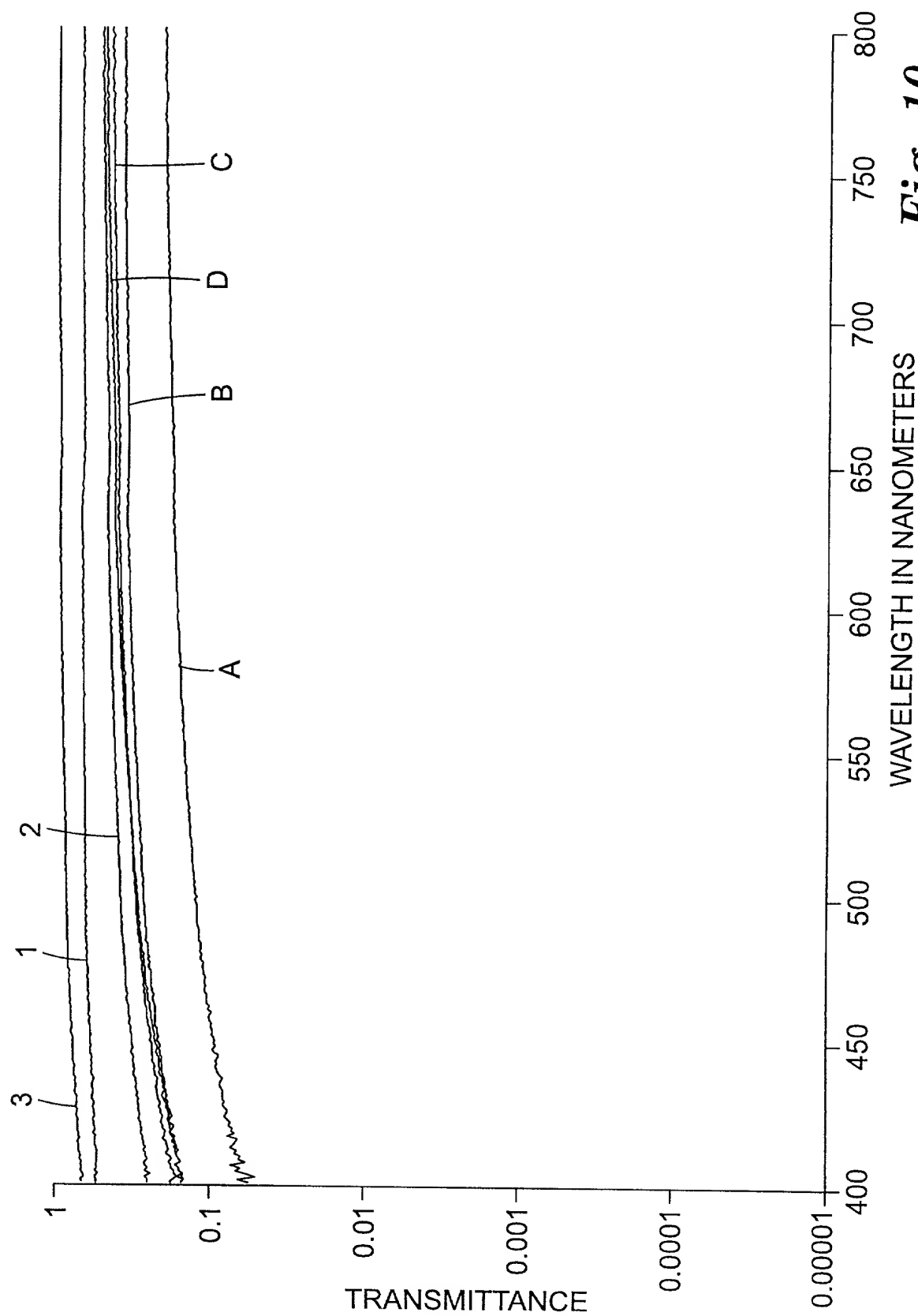


Fig. 10

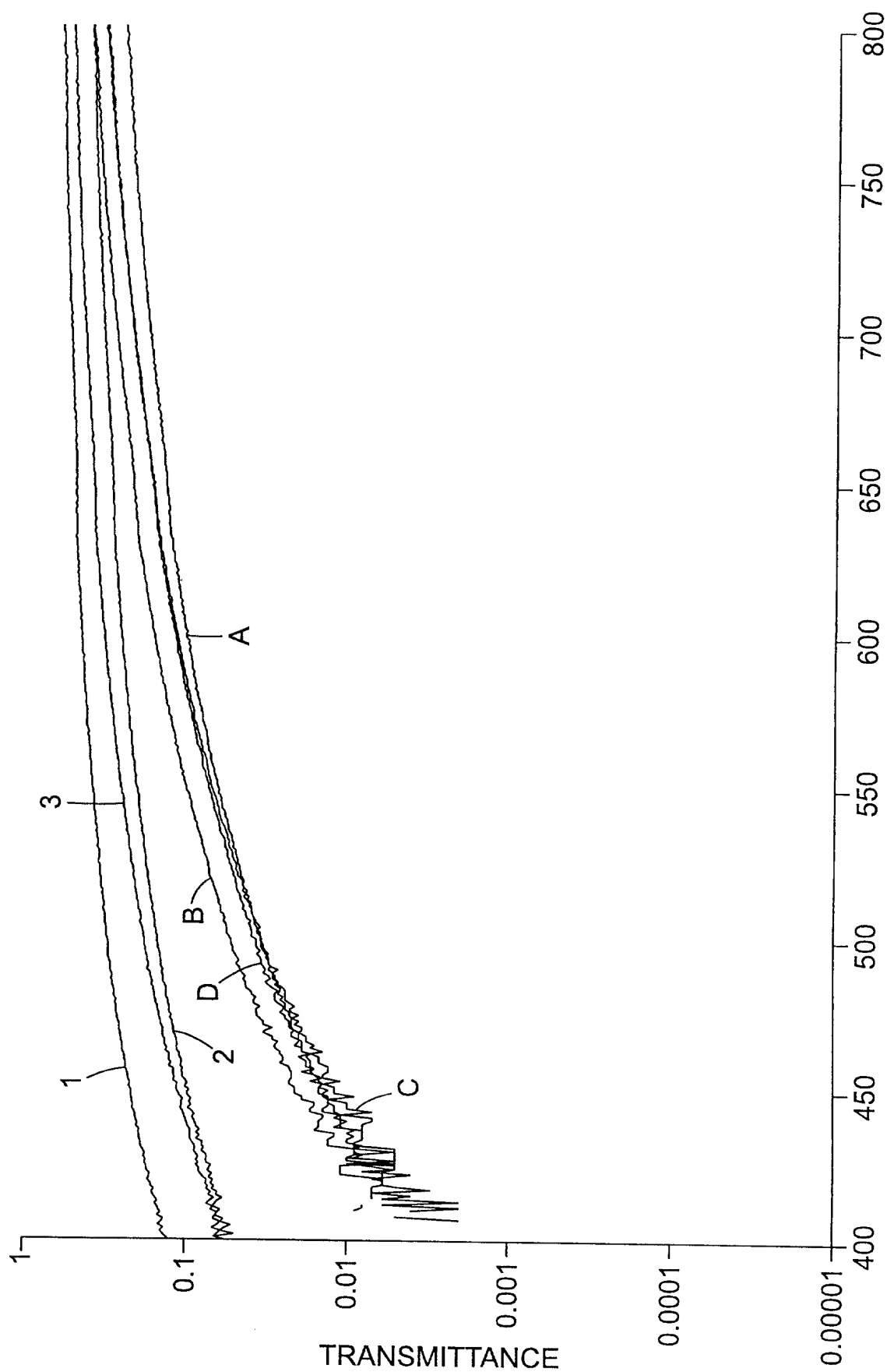


Fig. 11

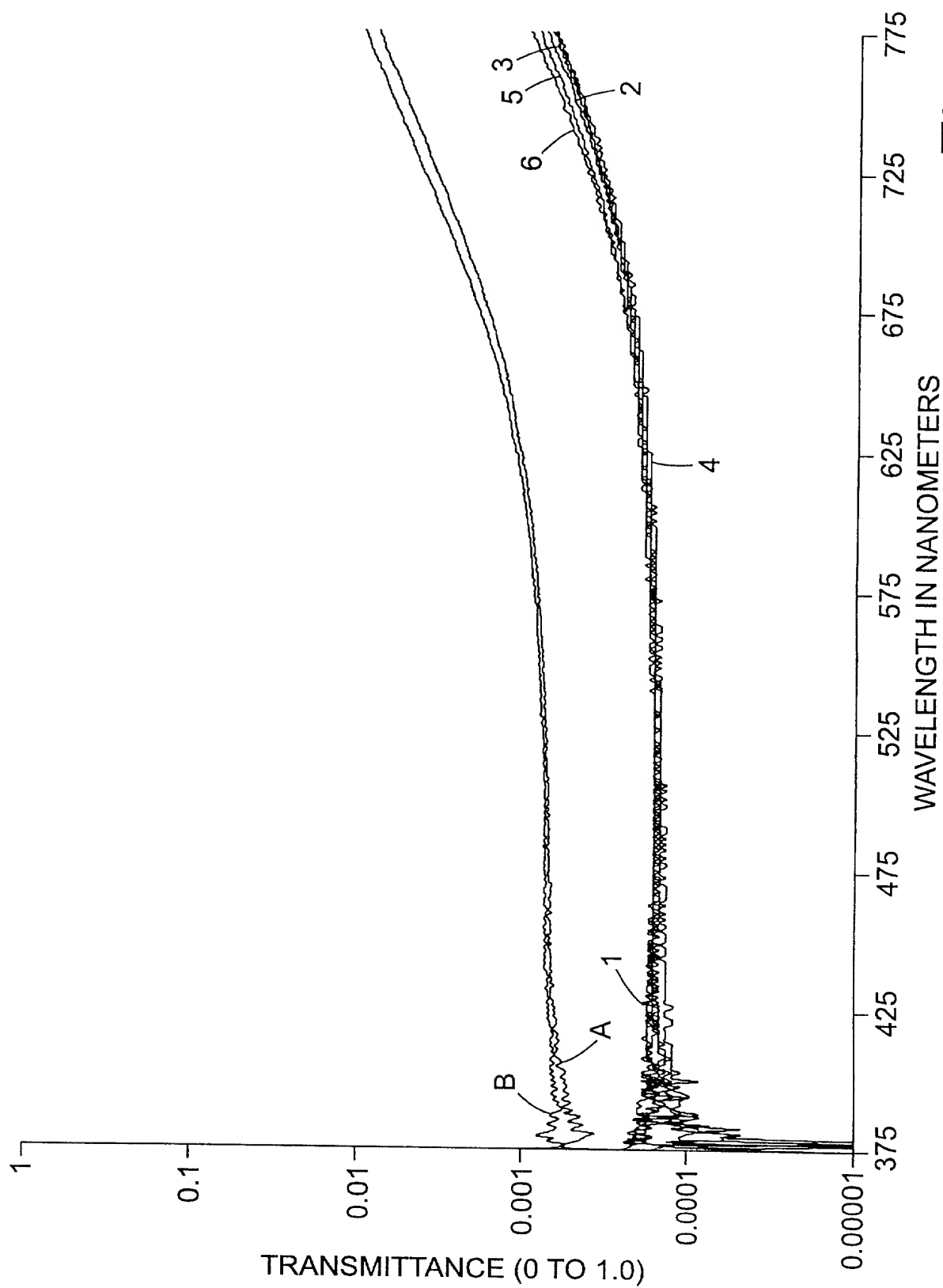


Fig. 12

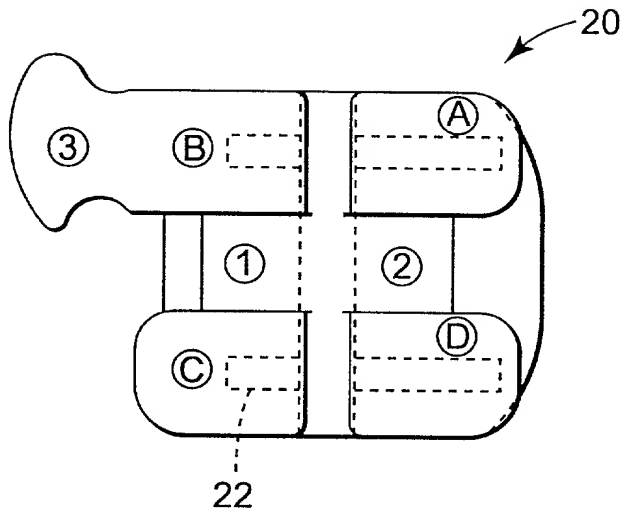


Fig. 13

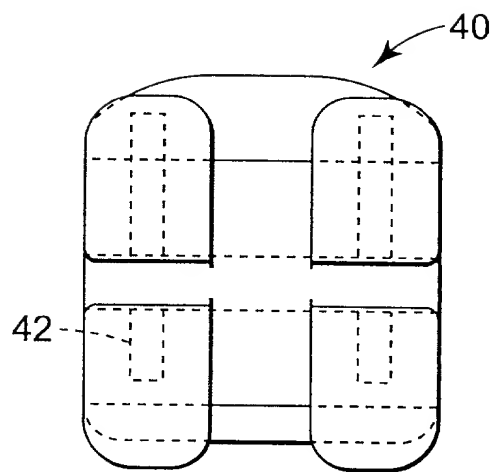


Fig. 14

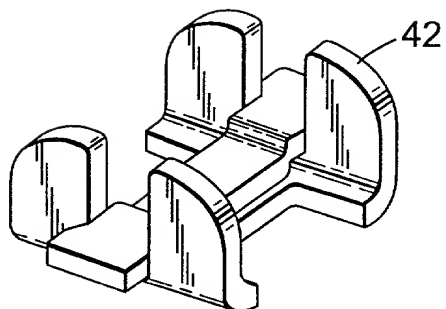


Fig. 15

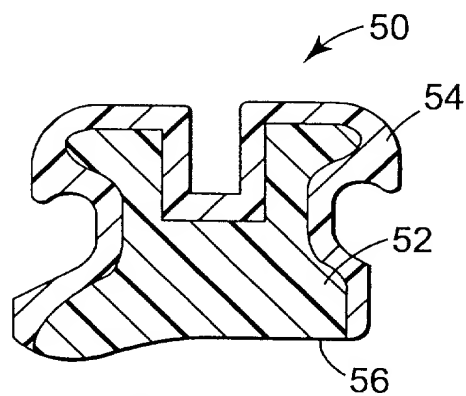


Fig. 16

DECLARATION, POWER OF ATTORNEY, AND PETITION

I, a below named inventor, depose and say that: (1) my residence, citizenship, and mailing address are indicated below; (2) I have reviewed and understand the contents of attached specification, including the claims, as amended by any amendment specifically referred to herein, (3) I believe that the other below named inventors and I are the original, first, and joint inventors or discoverers of the invention or discovery in

FLUOROPOLYMERIC ORTHODONTIC ARTICLE

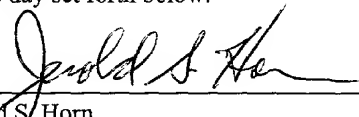
described and claimed therein and for which a patent is sought; and (4) I hereby acknowledge my duty to disclose to the Patent and Trademark Office all information known to me to be material to the patentability as defined in Title 37, Code of Federal Regulations, §1.56.*


I hereby appoint Gregory D. Allen (Reg. No. 35,048), Scott A. Bardell (Reg. No. 39,594), Carolyn A. Bates (Reg. No. 27,853), Stephen W. Bauer (Reg. No. 32,192), Dale A. Bjorkman (Reg. No. 33,084), Jennie G. Boeder (Reg. No. 28,952), William J. Bond (Reg. No. 32,400), Stephen W. Buckingham (Reg. No. 30,035), Paul W. Busse (Reg. No. 32,403), Gerald F. Chernivec (Reg. No. 26,537), James D. Christoff (Reg. No. 31,492), David R. Cleveland (Reg. No. 29,524), Philip Y. Dahl (Reg. No. 36,115), Janice L. Dowdall (Reg. No. 31,201), Lisa M. Fagan (Reg. No. 40,601), Darla P. Fonseca (Reg. No. 31,783), John A. Fortkort (Reg. No. 38,454), Matthew J. Goggin (Reg. No. P-44,125), Melanie G. Gover (Reg. No. 41,793), Gary L. Griswold (Reg. No. 25,396), Doreen S. L. Gwin (Reg. No. 35,580), H. Sanders Gwin (Reg. No. 33,242), Michaele A. Hakamaki (Reg. No. 40,011), Karl G. Hanson (Reg. No. 32,900), Nestér F. Ho (Reg. No. 39,460), Jeffrey J. Hohenshell (Reg. No. 34,109), Robert W. Hoke (Reg. No. 29,226), John H. Hornickel (Reg. No. 29,393), MarySusan Howard (Reg. No. 38,729), Stephen C. Jensen (Reg. No. 35,207), Robert H. Jordan (Reg. No. 31,973), Harold C. Knecht III (Reg. No. 35,576), Kent S. Kokko (Reg. No. 33,931), Charles D. Levine (Reg. No. 32,477), Douglas B. Little (Reg. No. 28,439), Eloise J. Maki (Reg. No. 33,418), Lisa M. McGeehan (Reg. No. 41,185), Matthew B. McNutt (Reg. No. 39,766), Michelle M. Michel (Reg. No. 33,968), William D. Miller (Reg. No. 37,988), Peter L. Olson (Reg. No. 35,308), Daniel R. Pastirik (Reg. No. 33,025), David B. Patchett (Reg. No. 39,326), Carolyn V. Peters (Reg. No. 33,271), Scott R. Pribnow (P-43,869), Terryl K. Qualey (Reg. No. 25,148), Ted K. Ringsred (Reg. No. 35,658), James A. Rogers (Reg. No. 37,228), Daniel C. Schulte (Reg. No. 40,160), Steven E. Skolnick (Reg. No. 33,789), Robert W. Sprague (Reg. No. 30,497), Brian E. Szymanski (Reg. No. 39,523), James J. Trussell (Reg. No. 37,251), F. Andrew Ubel (Reg. No. 36,704), and Lucy C. Weiss (Reg. No. 32,834), my attorneys and/or agents with full powers (including the powers of appointment, substitution, and revocation) to prosecute this application and any division, continuation, continuation-in-part, reexamination, or reissue thereof, and to transact all business in the Patent and Trademark Office connected therewith; the mailing address and the telephone number of the above-mentioned attorneys and/or agents are

Attention: James D. Christoff
3M Office of Intellectual Property Counsel
P.O. Box 33427
St. Paul, Minnesota 55133-3427
Telephone No. 651/733-1512

The undersigned petitioner declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Wherefore, I pray for grant of Letters Patent for the invention or discovery described and claimed in the attached specification and we hereby subscribe our names to the foregoing specification and claims, declaration, power of attorney, and this petition, on the day set forth below.


Jerold S. Horn
Residence: Los Angeles, California, United States of America
Citizenship: USA
Post Office: P.O. Box 33427
Address: St. Paul, Minnesota 55133-3427


Date

*Title 37, Code of Federal Regulations, §1.56 is attached.

03062629 "030499

James D. Hansen
James D. Hansen

Date _____

James D. Hansen

Residence: Pasadena, California, United States of America

Citizenship: USA

Post Office P.O. Box 33427

Address: St. Paul, Minnesota 55133-3427

(a) A patent by its very nature is affected with a public interest. The public interest is best served, and the most effective patent examination occurs when, at the time an application is being examined, the Office is aware of and evaluates the teachings of all information material to patentability. Each individual associated with the filing and prosecution of a patent application has a duty of candor and good faith in dealing with the Office, which includes a duty to disclose to the Office all information known to that individual to be material to patentability as defined in this section. The duty to disclose information exists with respect to each pending claim until the claim is cancelled or withdrawn from consideration, or the application becomes abandoned. Information material to the patentability of a claim that is cancelled or withdrawn from consideration need not be submitted if the information is not material to the patentability of any claim remaining under consideration in the application. There is no duty to submit information which is not material to the patentability of any existing claim. The duty to disclose all information known to be material to patentability is deemed to be satisfied if all information known to be material to patentability of any claim issued in a patent was cited by the Office or submitted to the Office in the manner prescribed by §§ 1.97(b)-(d) and 1.98. However, no patent will be granted on an application in connection with which fraud on the Office was practiced or attempted or the duty of disclosure was violated through bad faith or intentional misconduct. The Office encourages applicants to carefully examine:

- (b) Under this section, information is material to patentability when it is not cumulative to information already of record or being made of record in the application, and

- A prima facie case of unpatentability is established when the information compels a conclusion that a claim is unpatentable under the preponderance of evidence, burden-of-proof standard, giving each term in the claim its broadest reasonable construction consistent with the specification, and before any consideration is given to evidence which may be submitted in an attempt to establish a contrary conclusion of patentability.

- (1) Each inventor named in the application;
- (2) Each attorney or agent who prepares or prosecutes the application; and
- (3) Every other person who is substantively involved in the preparation or prosecution of the application and who is associated with the inventor, with the assignee or with anyone to whom there is an assignment to assign the application.

(d) Individuals other than the attorney, agent or inventor may comply with this section by disclosing information to the attorney, agent, or inventor.